

PLASMA CHEMISTRY  
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The capability of a plasma to produce high temperatures, activated species and electromagnetic radiations, offers the chemist and chemical engineer another tool for the laboratory and processing plant. These characteristics of the plasma are potentially useful if the thermodynamics of the reaction under consideration permit, and they are actually useful only if the kinetic parameters can be controlled. These, then, are the necessary and sufficient conditions to permit economical exploitation of plasma chemistry. By and large, thermodynamic data are readily available, but the kinetics of reactions at very high temperatures are almost unknown. Therefore, the area of plasma chemistry research resolves into the study of kinetic parameters such as temperature, pressure, flow rates, and residence times in zones of specific temperatures, etc.

Plasmas are most often generated by means of electric arcs, radio frequency induction, microwaves, and low frequency induction in the range of 1500 cycles/second.

The greatest amount of study for commercial exploitation has been done with the arc plasma. The others, as yet, have not been fully developed to be economically operable, although improvements are continually being

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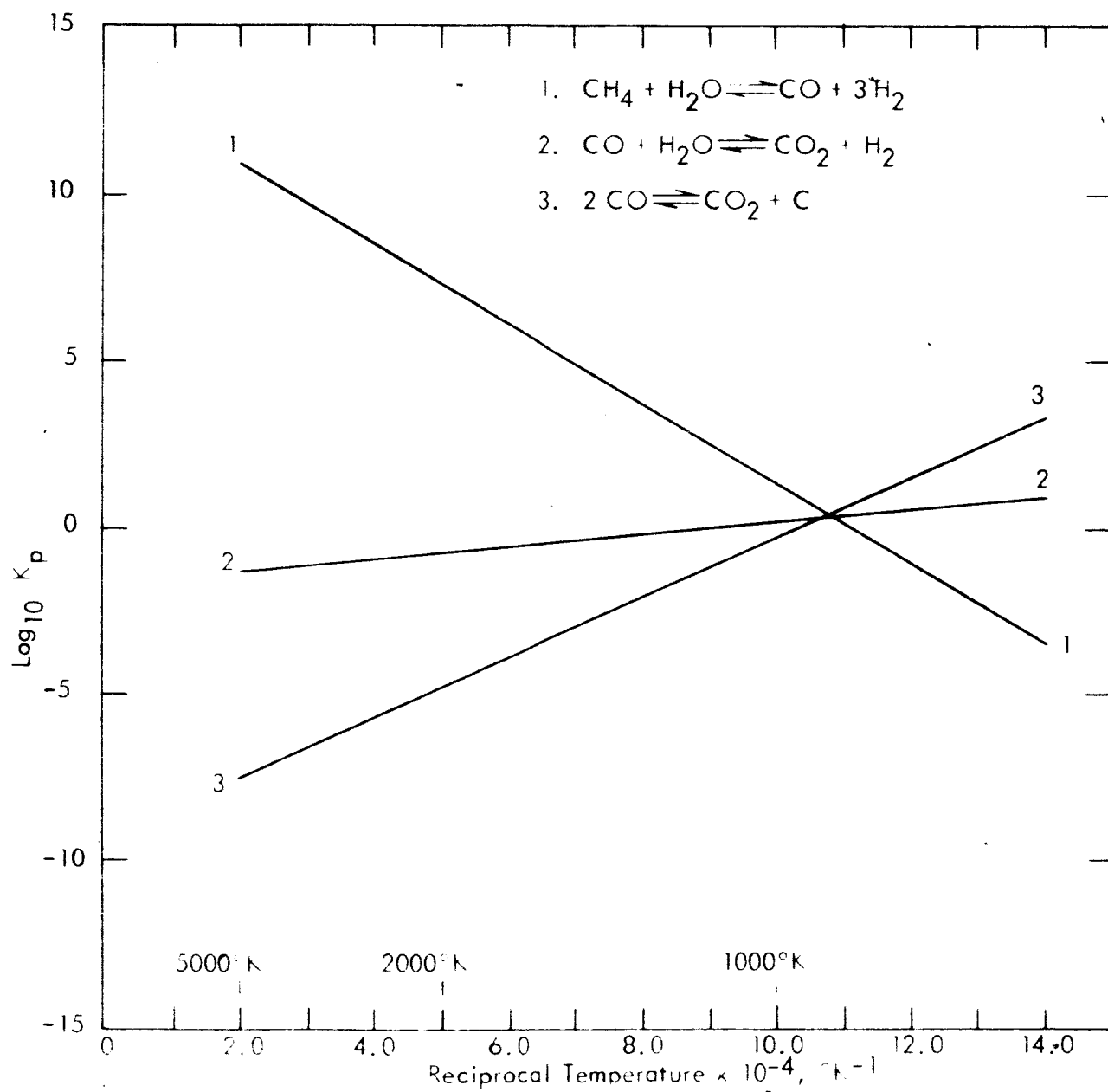
made. Since the characteristics of plasmas generated by different means are matters of degree rather than kind, the following discussions based on arc plasma technology will be generally applicable to all plasmas. A specific organic, a specific inorganic reaction and a method of utilizing the electromagnetic radiation of the arc plasma will be described.

### ORGANIC REACTION

The organic reaction to be discussed is steam reforming with methane to produce carbon monoxide and hydrogen gas. The conversion of methane to hydrogen by thermal reaction can be represented by the three independent equations as shown in Figure 1. Reaction 1 is endothermic and reaction 2 is exothermic.

A plot of  $\log K_1$ ,  $K_2$ , and  $K_3$  vs. reciprocal temperature is also shown. It can be seen that reactions 2 and 3 are suppressed at high temperatures while reaction 1 is enhanced at high temperatures. This is an ideal situation for the plasmajet reactor if a product gas with little or no  $\text{CO}_2$  in it is desired (which is usually the case). Operation of the reactor at a high temperature level (above  $2000^\circ\text{K}$ ) would both suppress the production of  $\text{CO}_2$  and the laydown of carbon, and would provide for a rapid reaction rate for reaction 1.

In general, reaction 1 is favored by high temperature, low pressure, and a high steam-carbon ratio; while reaction 2 is favored by low temperature, high steam-carbon ratio, and is unaffected by pressure. The usual proce-



# PLASMAJET STEAM-METHANE REFORMING

Figure 1

ture in steam-methane reforming is to promote reaction 1 at 1000°C in the presence of an aluminum oxide catalyst. More steam is then added to the CO and H<sub>2</sub> mixture from this reaction and reaction 2 is promoted in the presence of an iron-base catalyst at 450 to 500°C. The resulting gas product is about 80% H<sub>2</sub> and 20% CO<sub>2</sub>. For most purposes, the CO<sub>2</sub> must be scrubbed from this gas before the H<sub>2</sub> is used.

In plasmajet-methane reforming, the operating temperature could be chosen high enough to obviate the use of a catalyst, and reaction 1 alone would be promoted. This could eliminate many equipment problems now encountered with conventional reforming equipment, particularly in the reactor section of the process.

Use of the plasmajet at high temperatures would also eliminate the use of excess steam and the necessity for its removal from the system downstream from the reaction, where it is usually scrubbed out along with CO<sub>2</sub> in conventional operations.

While methane has here been chosen to illustrate the potential of steam reforming with the plasmajet, other light hydrocarbons are equally suitable feedstock for plasmajet-steam reforming. The thermodynamic considerations discussed, in general, also apply to other steam-reforming reactions.

In summary, plasmajet steam reforming of light hydrocarbons is thermodynamically feasible, resulting in the production of a reducer gas consisting

primarily of  $H_2$  and  $CO$ , and essentially uncontaminated with  $CO_2$  and steam.

Economically it can be shown that the cost to process one pound each of methane and water vapor amounts to approximately one cent. This figure is obtained by adding the BTU/lb required to heat each reactant to  $1500^\circ K$  and converting to kilowatts. A sample calculation is shown:

1150 BTU/lb to heat $H_2O$ to $1500^\circ K$
2091 BTU/lb to heat $CH_4$ to $1500^\circ K$
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3241 BTU/2lb. reactants

Assume feed rate of 0.2 lb/second

Then: 0.2lb/second  $\sim$  350 KW into gas

Assume 50% efficiency for reactor

Then: 0.2lb/second  $\sim$  700 KW input

In one hour, 720 lb can be processed for 700 KWH. Assume cost of power to be 1 cent/KWH (for simplicity).

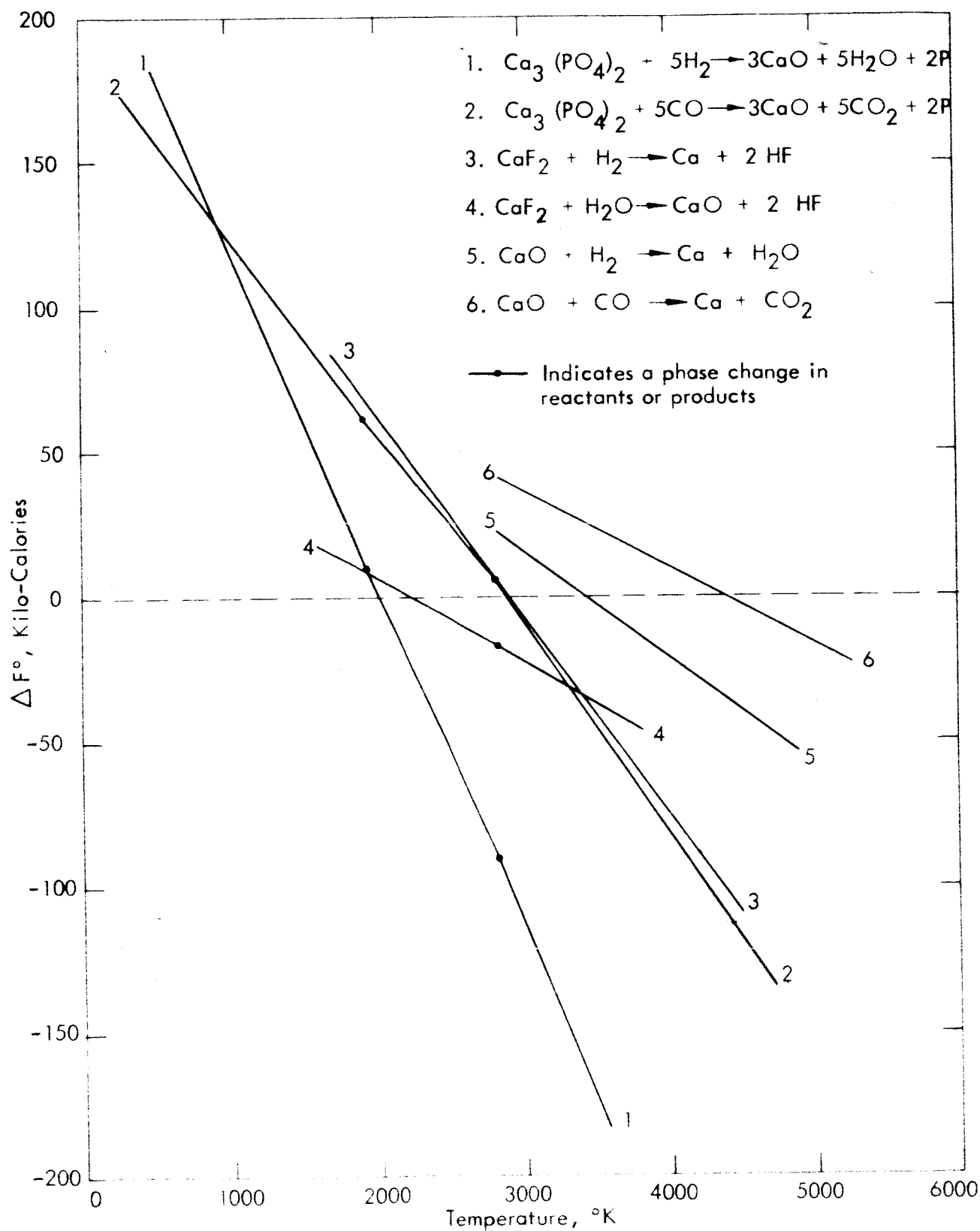
Then: $\frac{720 \text{ lb/hr}}{700 \text{ KWH at 1 cent/KWH}}$	$\approx$ 1 cent per 2lbs of reactant
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### INORGANIC REACTION

It is suggested that the reducer gas be used in a plasma to reduce phosphate rock directly to elemental phosphorus. The current electric furnace process for producing phosphorus involves the use of a considerable amount

of hardware. In addition, considerable amounts of heat are lost in melting the siliceous flux used in the furnaces. The proposed plasma process for the production of phosphorus is shown in Figure 2. The phosphate rock (fluorapatite) is shown as a mixture of calcium phosphate and calcium fluoride. There are six competing reactions to be considered. Reactions 1 and 2, of course, are the desired ones. Of these six, reactions 5 and 6 can be eliminated by reducing the effective temperature to below  $3400^{\circ}\text{K}$ ; at which temperature free energy considerations would not permit reactions 5 and 6 to occur. As stated earlier, this effective temperature can be obtained by controlling the residence time of the particles in the arc gas or by introducing the reactants with additional cold gas in a plenum chamber downstream of the arc. Further examination indicates that the reactions should be carried out at temperatures above  $2100^{\circ}\text{K}$ . This then gives a  $1300^{\circ}$  bracket in which to carry out the operation. Unfortunately, in this bracket reactions 3 and 4, which are completely undesirable, will also occur. There then remain two means by which the elemental phosphorus can be recovered without contamination. The first depends on the kinetics of reactions 1 and 2 being faster than those of reactions 3 and 4. If this is the case, no further controls will be necessary. However, this must be determined experimentally. If it should develop that the rates of reactions of these first four reactions are of the same order of magnitude, then scrubbing and other separating techniques must be incorporated to recover the elemental phosphorus in a pure form.

Thus, a process utilizing the synthesis of reducer gas which is then sub-



PLASMAJET PHOSPHORUS REDUCTION  
Figure 2

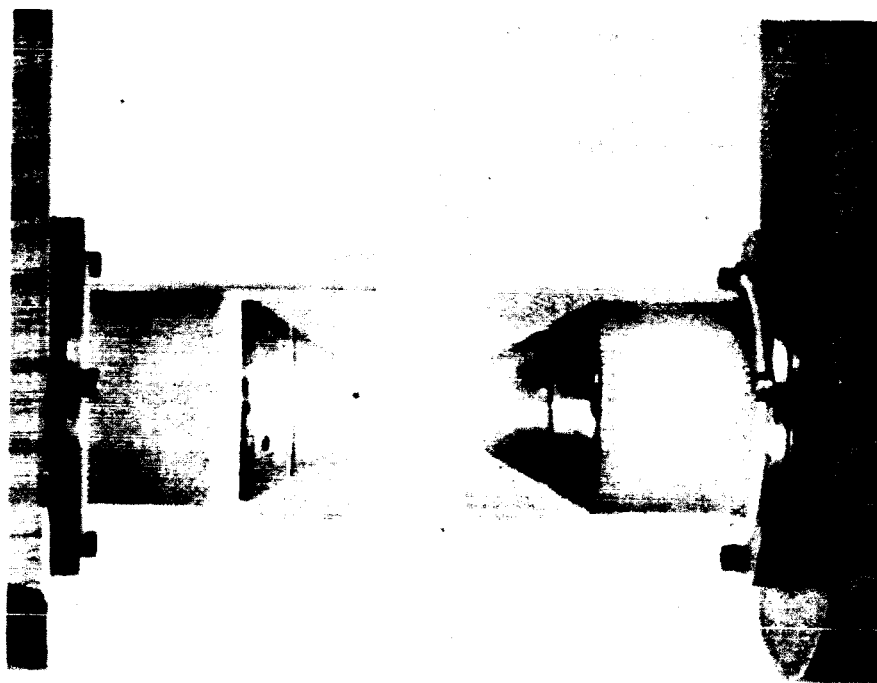
sequently used to reduce phosphate rock to elemental phosphorus has been described. It is conceivable that in the final development the working device which will be a system of multiple arcs and chambers will be about the size of a breadbox.

The considerations given to the phosphorus process of course can be applied to other inorganic processes such as the reduction of ores to metals. Such reactions have been carried out at Plasmadyne Corporation. Among other organic reactions being considered are the cracking of hydrocarbons, oxidation of propylene and ammonia to form acrylonitrile, the direct oxidation of benzene to phenol utilizing short residence times followed by quick quenching, and others. Before leaving a discussion of the purely thermal characteristics of the plasma arc, it should be mentioned that the plasma completely aside from being involved in any chemical synthesis can be used as a fast heater or preheater for gases to be used in certain processes.

### ELECTROMAGNETIC RADIATION

The one facet of arc plasmas that has generally been ignored is its usefulness to produce intense electromagnetic radiation. A vortex stabilized radiation source has been developed, which is shown in Figure 3. The unit consists of a fused silica cylinder and two water-cooled conical electrodes aligned on a common axis. The working gas is introduced tangentially to the inside circumference of a fused silica cylinder and forms a vortex as it spins to the central axis exhausting through a drilled





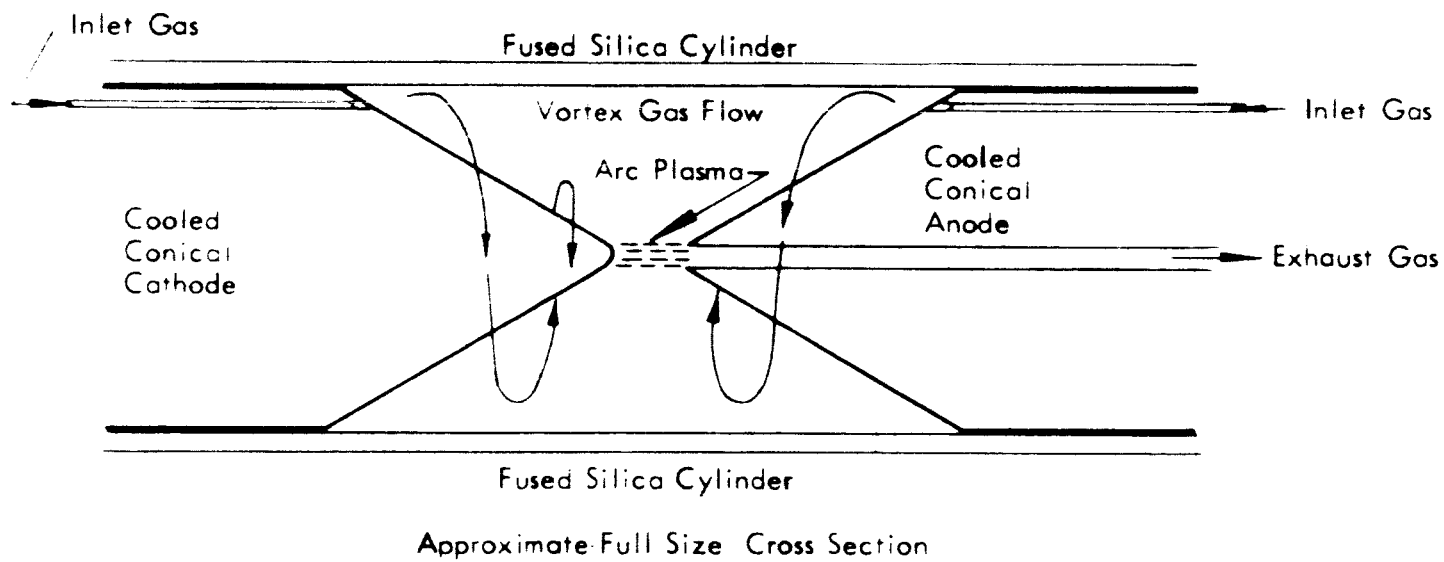
# **VORTEX STABILIZED RADIATION SOURCE**

**Figure 3**

hole at the anode tip. A schematic cross-section of this device is shown in Figure 4. The vortex action of the gas serves two purposes in that it continues the plasma to a thin cylinder, essentially the diameter of the exhaust hole and secondly, it serves to absorb infrared radiation which leaves the fused silica cylinder envelope rather cool to the touch after operation. Since the transparent envelope is sealed to the copper electrodes by O-rings or a Teflon sleeve, the gases can be introduced under pressure and with high power inputs. This source presents significant technological advances in four important areas as follows:

1. The source unit can use a variety of gases or mixtures of gases. This feature permits control of spectral energy distribution in the radiation produced.
2. Units can be designed for very large power inputs and operation over a wide range of power levels.
3. The cool vortex flow continually replaces the gas surrounding the arc, thus reducing greatly red and infrared radiation when compared to other short arc sources. Also, the vortex fixes the arc plasma diameter and precisely locates the arc column. Further, no reaction occurs between the gases and the envelope to discolor the envelope, such as occurs with metal vapor lamps.
4. The unit can be built to operate in any attitude and in any environment from a liquid such as sea water to the vacuum of space.

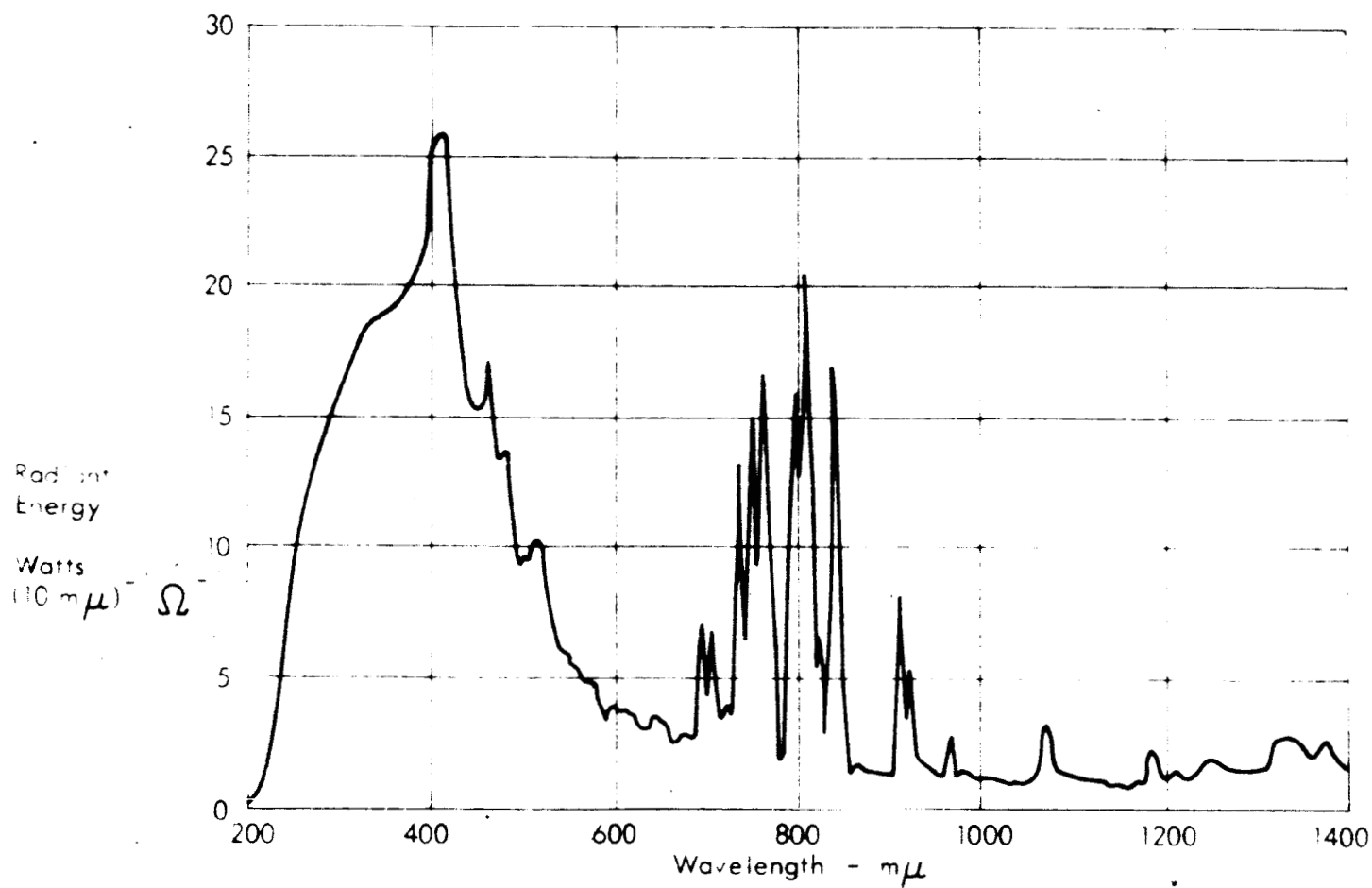
This unit has been successfully operated with argon, helium, nitrogen,



## VORTEX STABILIZED RADIATION SOURCE

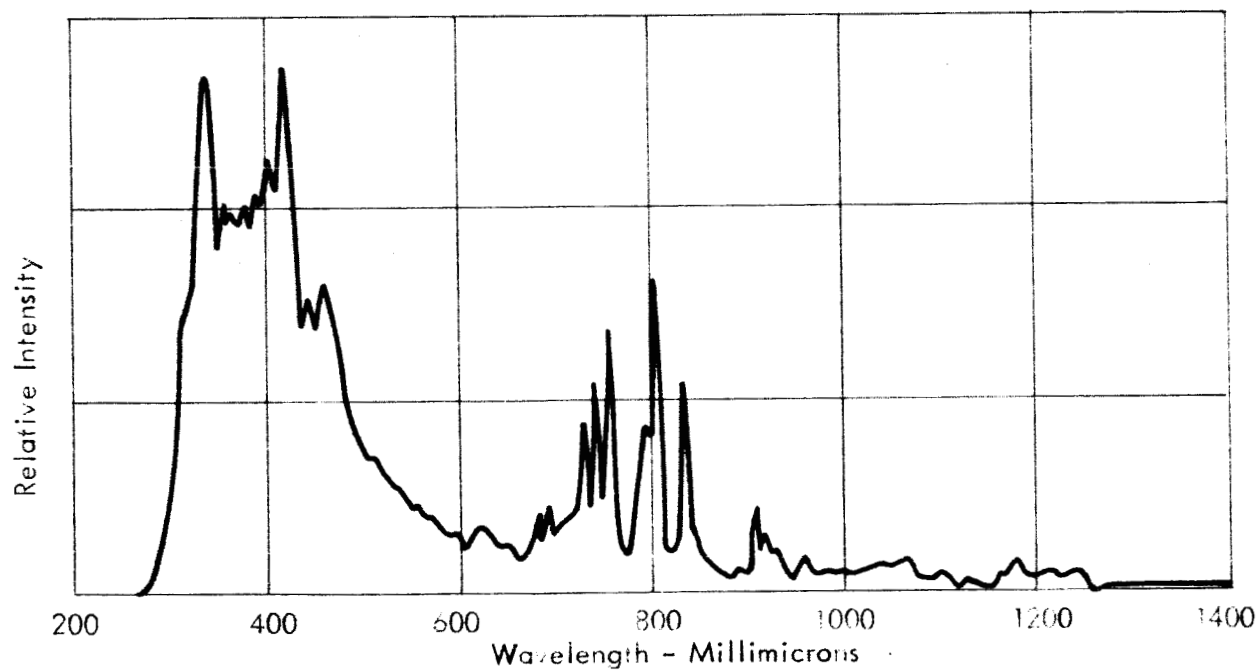
Figure 4

and argon-neon mixtures. Operation with argon is of particular interest to the chemists since the radiation output has a very high ultraviolet intensity. Figure 5 shows the spectral energy distribution with argon at a power input of 25 KW. The arc chamber pressure was 17 atm. The total radiant flux output of 7.68 KW represents a 31% efficiency in conversion of electrical power to radiant energy. Of these 7.68 KW, 2.6 KW were found in the 2000 to 4000°A range. Comparing the ultraviolet peak at slightly over 4000°A to the high peak of approximately 8000°A in the red, indicates a UV to IR ratio of approximately 1.25. Figure 6 shows the spectral distribution using argon but at a power input of 97 KW. Here we see the UV to IR ratio has increased to approximately 1.7. To the chemist or chemical engineer then, this device becomes a powerful tool with which to conduct photochemical reactions of low quantum yield for which high intensity radiation is necessary. Areas of reactions which are being pursued at this time include halogenation, oxidation, reduction, polymerization without the use of catalysts, decomposition, and chemical synthesis. These photochemical applications are still in the development stage and therefore few data are available. A few exploratory studies have been made simply to prove that such reactions are possible. Some of the reactions shown to be possible are: 1) Polymerization of some solid rocket propellant binders, 2) formation of a thin polymer skin on Penton monomer, 3) degradation of plastic materials by exposure to the intense ultraviolet light, 4) the production of ozone in the atmosphere surrounding the lamp.



SPECTRAL ENERGY DISTRIBUTION - ARGON

Figure 5



UNCORRECTED MONOCHROMATOR RUN, 97 KW ARC

Figure 6

Photochemistry, of course, is the obvious application of such a high intensity lamp. Because the light is so intense very slow reactions may reach practical speeds. Photocopying methods may benefit from such a speed-up.

In view of the versatility of this apparatus in being able to accomodate mixtures of gases other applications immediately come to mind. Among these are the simulation of sunlight for solar simulation chambers. Since the light source is essentially a point source, its applicability to arc imaging furnaces is obvious. Another interesting possibility is the use of such a source to pump a laser device.

The above serve to illustrate the wide range potential of plasma technology. In addition to exploring the above reactions, Plasmadyne has proved the feasibility of applying the technology to 1) purification of oxides, 2) reduction of refractory metal salts, 3) reduction of scale on copper ingots, and 4) heating tonnage quantities of gases to high temperatures.

Although the uses of plasmas in chemical reactions and in other devices have been presented in a rather broad manner, it is felt that the potentials of such a high thermal and electromagnetic radiation source are essentially limitless. Some work has been done, but the surface of the possibilities has only been scratched. In the years to come, one can confidently expect plasma technology to take a significant and important role in chemical processing, particularly in processes which today are not possible by known methods.